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Final Report

WORK FUNCTION DETERMINATION OF PROMISING MATERIAL FOR THERMIONIC CONVERTERS

JPL Contract 955054

For Jet Propulsion Laboratory
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by

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"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology sponsored by the National Aeronautics and Space Administration under Contract NAS7-100 "

ERC-R-7903

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Abstract:

This final report describes the work done to fabricate Marchuk plasma discharge tubes for measurement of the cesiated emission of lanthanum hexaboride and thoriated tungsten electrodes. Repeated tube failures delayed the measurements and both materials. The effort with thoriated tungsten will be completed after the end of the program. A photon counting pyrometer was completed and will be in use during future measurements after calibration with a gold standard at Los Alamos Scientific Laboratory.

Summary:

The program during the past year was scheduled to determine experimentally, the cesiated emission of lanthanum hexaboride (LaB^6) and some thoriated tungsten alloys. The Marchuk tube prepared for the measurements failed on four different occasions, twice when emission measurements were being started. The failures were cracks in the tubes, one caused by a shorting out of the plasma cathode filament and the others were due to stress cracks resulting from the tube fabrication. Successful tubes have been built in the past with Corning type 7052 glass. The cesium temperature of 412 K with a probe temperature 1200 K were found, to be near the compatability limit of the 7052 glass. The effort this past year included the incorporation of tube glass with higher temperature capability and greater resistance to cesium attack. This endeavor certainly led to fabrication problems on the new tubes. Both Uranium glass and a special German glass, Jena glass were used for this purpose. It is felt that the fabrication experience will now lead to successful experiments.

A photon-counting pyrometer has been built and tested and needs only to be standardized at LASL prior to incorporation into the experimental plasma tube measurements.

OBJECTIVES

The objective of this work was to perform cesiated emission measurements on lanthanum hexaboride and thoriated tungsten and to calculate work functions and obtain other properties pertinent to thermionics converters operating with an emitter temperature of 1650 K.

Marchuk Tube Fabrication

The search for a optimum glass envelope has been ongoing since the first program started two years ago. Three glasses have been chosen

as promising candidates, Corning 1720, and 3320, and Jena glass which is imported from Germany. The Jena is suppose to be the best alternative with 1720 next. A minimum of $1,500 was required for the Corning 1720 tubes in the three sizes required. Attempts to place a smaller order or get some free samples were unsuccessful. The ASU glass shop had a small quantity of 3320, or so-called Uranium glass and this was thus used to construct the marchuk tubes for this program.

Both 1720 and Jena glass were purchased and tubes were fabricated.

Construction of a Marchuk tube can be divided into a number of elements:

1. Prepare seals for tungsten wire lead-throughs.
2. Electron discharge machine molybdenum bushings for probe wire spacers.
3. Prepare sample wires (if LaB_6, rhenium wires must be coated).
4. Spot weld probes, collector and emitter to the tungsten leads.
5. Make guard rings on the tube by coating the glass with liquid bright platinum.
6. Paint exposed metal parts with alumina powder to eliminate possible emission areas.
7. Assemble component parts.

Seals are made by first oxidizing the tungsten wires and then sealing them to the glass. This task requires close-dimensioning and demands careful work with the result that, a few faulty ones were still made and had to be discarded.

Construction of the experimental Marchuk tube required fabrication of small bushings. The bushings are 1/8 inch in length 0.049 inch O.D., and 0.014 inch O.D., and are necessary to hold and center the probe wire in the ceramic insulator. This prevents the test emitter loop from touching the insulator and thus reducing its true temperature.

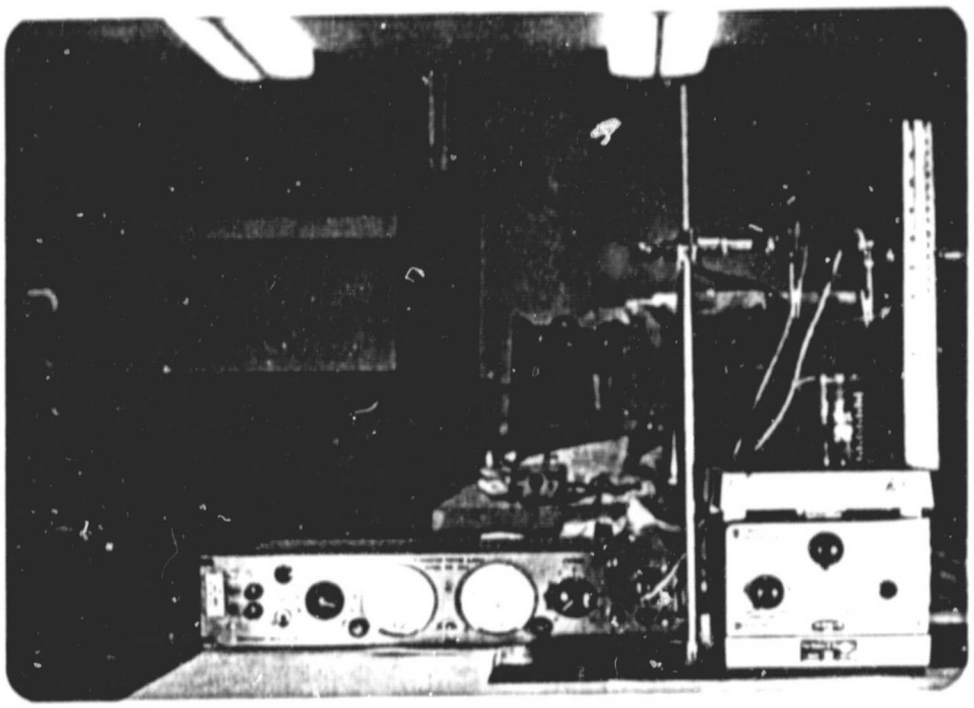
Stainless steel hypodermic tubes were first used to make these bushings. Since they come in set sizes, three were needed to meet the required O.D. and I.D. However, they didn't hold together well and there was difficulty in assembling them. It was recognized also that stainless steel would not be a good material to be used in this experiment because of its composition and associated the high vapor pressure. Molybdenum was chosen for this application.

The hardness of molybdenum makes conventional machining extremely difficult. Electrical-discharge machining (EDM) is time consuming and expensive, but is a successful method. Machinists at the ASU Engineering Shop prepared a special jig for machining. The bushings were completed after considerable effort.

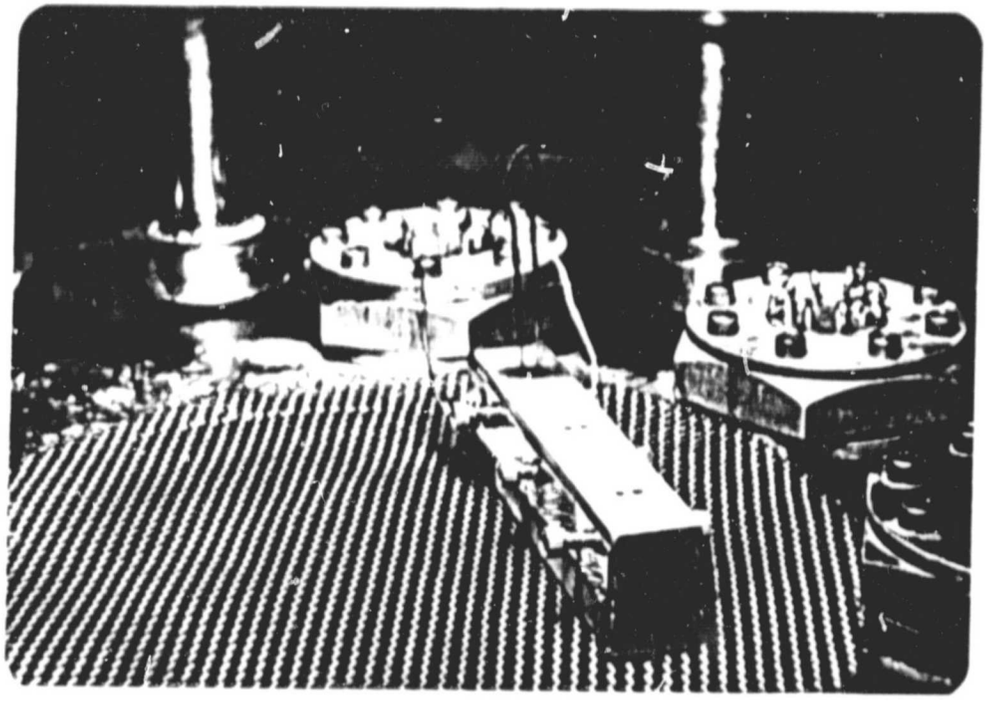
The rhenium wire was coated with lanthanum hexaboride by a cataphoresis process refined in our laboratory.[1] Photograph 1 shows the set-up for such a process. Before and after the rhenium wire was coated, it was flashed in a vacuum. A jig to support up to 3 wires was made out of green lava, a soft ceramic that can be machined and then fired to get regular ceramic properties. A coated rhenium wire ready to be flashed in a vacuum bell-jar is shown in Photograph 2.

Buckingham[2] recommended that the LaB_6 have a particle size range of 5-8 μm. The LaB_6 purchased from Cerac Inc. is about 325 mesh (44 μm). Although a coating can be formed, it was found that it flaked off very easily even after it had been sintered in vacuum. The LaB_6 was ground to obtain very fine particles. The smaller particle size coating did not shown any tendency to fall apart. LaB_6 supplied by JENA was successfully coated on the rhenium substrate. The tube containing probes of Ni, $LaB_{7.4}$ and $LaB_{6.5}$ was prepared.

The main problem encountered was that once the probes are flashed in vacuum, the coatings tend to crack and distort, making the surface area determination quite difficult. The rhenium appeared to remain covered but the coating became irregular. The normal procedure for determining surface area is by magnified photograph, and the irregular



Photograph 1 - Set-up for a cataphoresis process



Photograph 2 - Flashing coated rhenium wire in vacuum jar

covering makes this determination difficult. A number of test wires were coated to obtain parameters to reduce the coating thickness. Coatings were obtained in which the irregularities were reduced and are not considered to be significant.

The probes were mounted on press leads which utilized uranium glass transition tungsten lead-throughs. Four-lead presses were used to support and conduct current to a counterwound spiral tungsten wire cathode.

The probes are constructed as shown in Fig. 3. These probe wires are passed through double-holed alumina insulators and form small loops about 1 cm in diameter at one end. The length of each of the exposed loops is determined from photographic enlargments of the probe loops are known, and the emitting areas are thus calculated.

The probes are protected from leakage currents by guard rings and from discharge at the lead-through by ceramics.

The collector and emitter were spot-welded to the tungsten leads from the press seals. This is shown in photographs 4 and 5 respectively. Some difficulties were encountered when spot-welding thin rhenium and nickel wires to tungsten wires. By careful selection of electrodes a weld can be made. To strengthen the joint, an intermediate piece of nickel or tantalum foil helps. This is later coated with high purity aluminum oxide to minimize possible current collection. Photograph 6 shows a coated rhenium wire and the seal with the tungsten wires.

Guard rings are painted on the inside surfaces of the side tubes to collect stray currents which might flow along the glass walls. To do this a coating of Hanovia 05X liquid platinum-bright is applied, then air-dried and finally fired. The conditions needed for this process are fairly rigid. For example, the glass has to be very clean or even etched before applying the coating. Also, the first coat must be very thin. Next, it is allowed to dry for a long period of time,

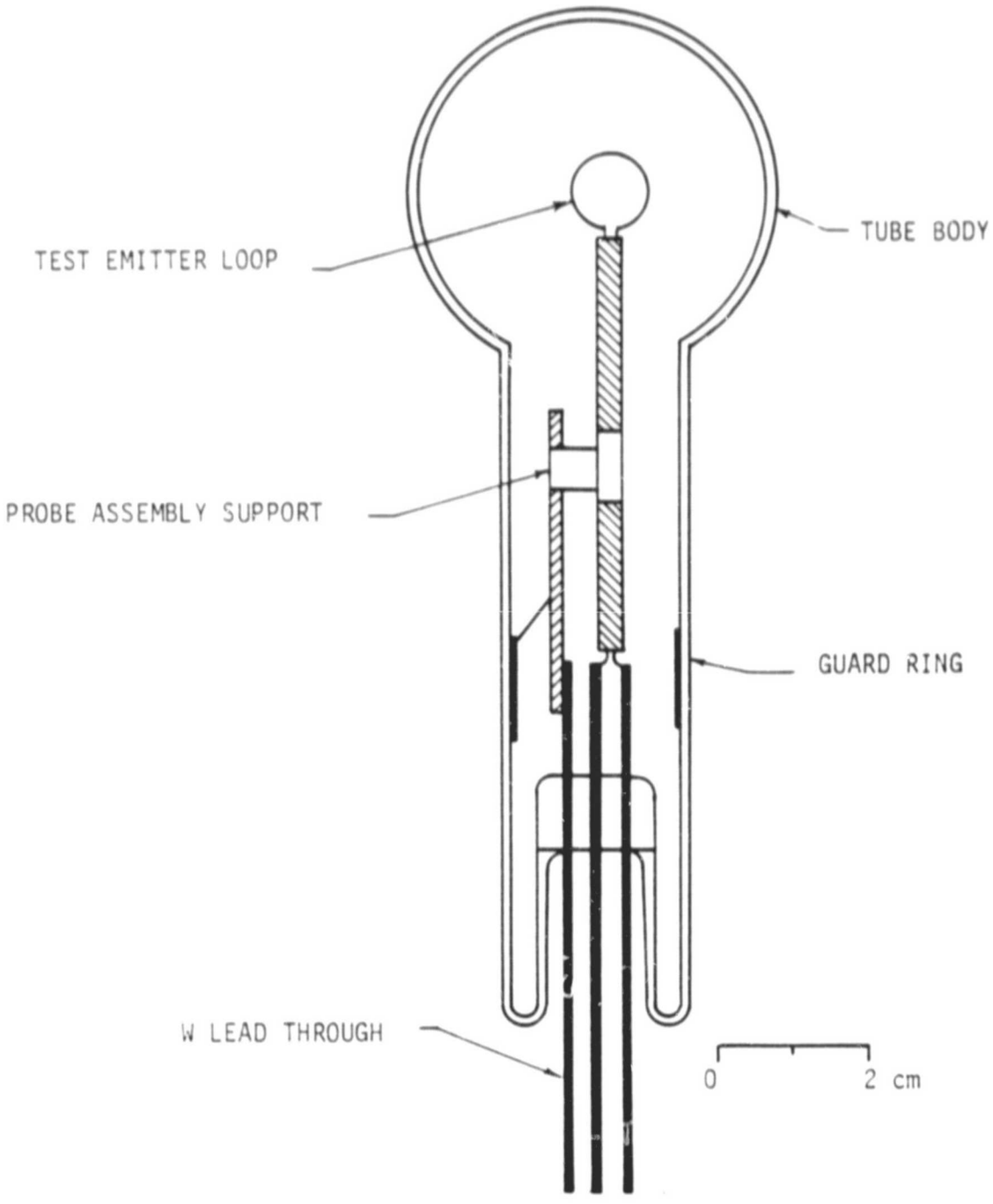
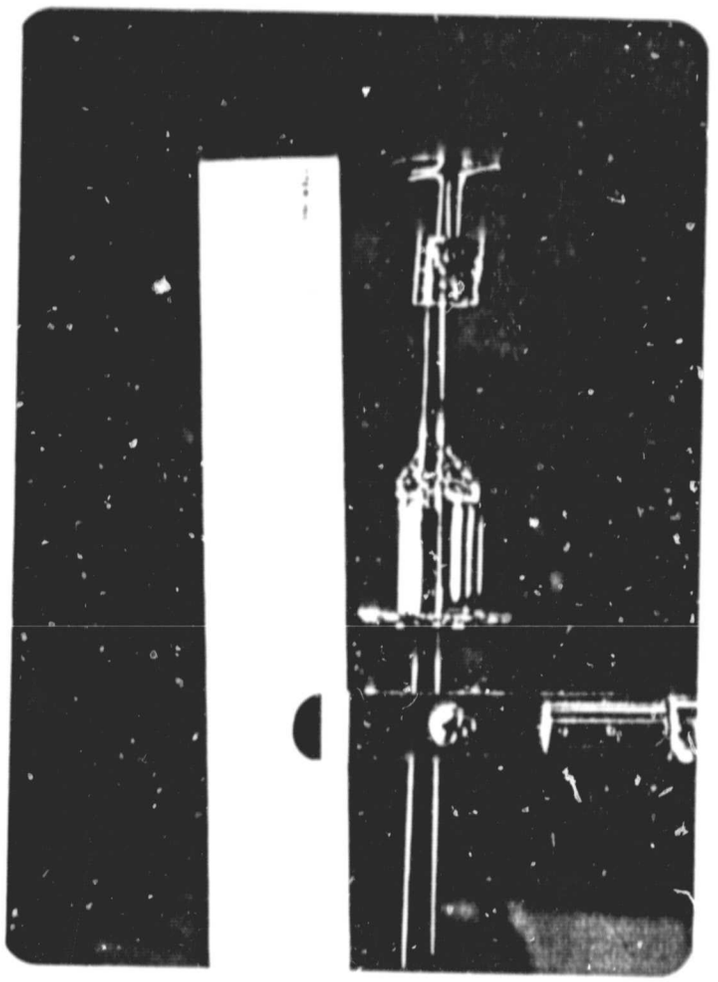
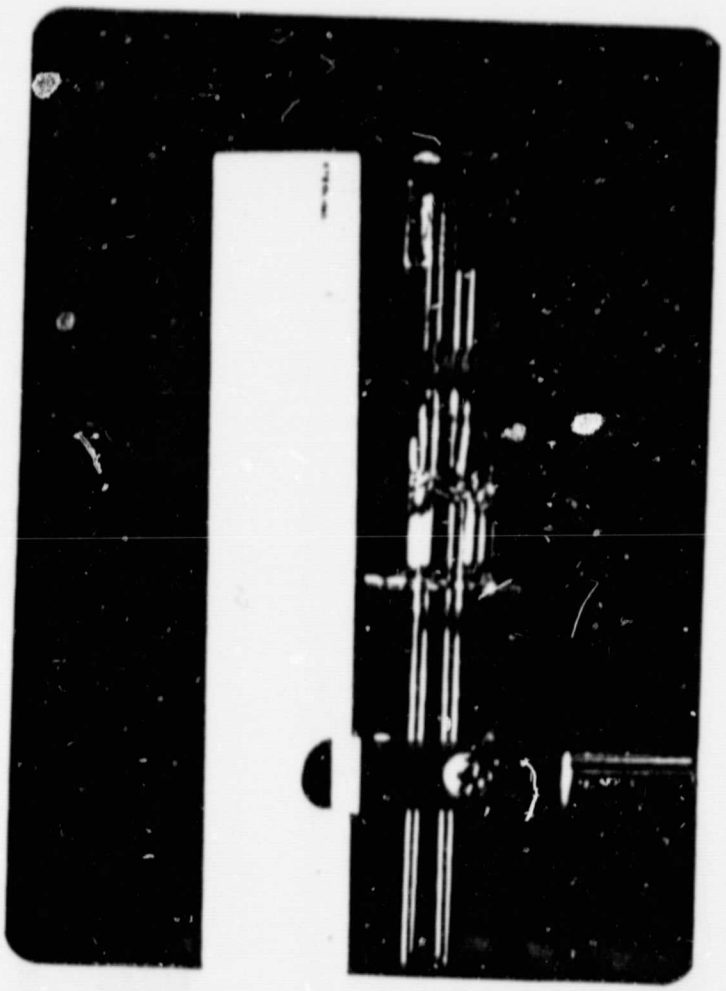


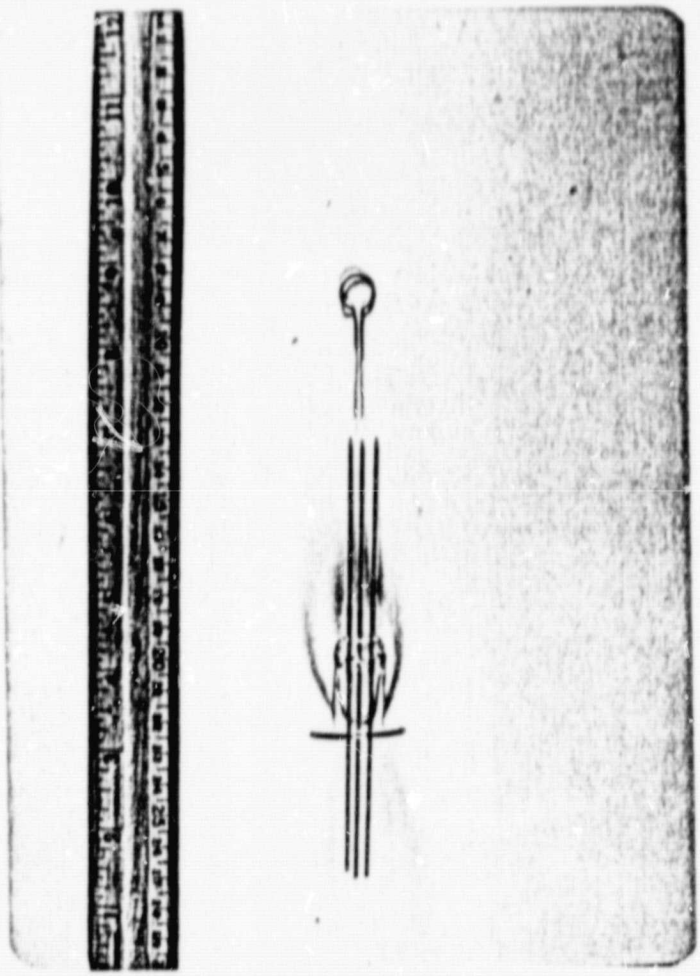
FIGURE 3 PROBE ASSEMBLY



Photograph 4 - Collector spot-welded to tungsten lead-throughs



Photograph 5 - Emitter spot-welded to tungsten lead-throughs



Photograph 6 - Coated rhenium with seal

preferably overnight. When firing it, there should be air flowing through the furnace until about 800 F. If either one of these conditions is not followed, the coating will flake off. Pyrex glass, since it is more readily available, was tried at first. After a few attempts the right method was finally achieved. At least two or three coats are needed. A good coating is one which is even, adheres to the glass surface well and is electrically conductive.

A number of steps have to be taken before each probe assembly can be put into the main tube. Close-up photographs of each probe wire tip were taken so that the area can be calculated accurately. A nickel wire was also spot-welded to the third tungsten lead-through and connected to the guard ring by a tantalum spring wire. Next, all exposed metal parts were painted with Norton 38-900 high-purity alumina powder. This minimizes possible current collection by these areas.

Finally, together with the collector and emitter, the probe wires were assembled into the main tube shown in Fig. 7. This is followed by connecting a cesium reservoir and a flange, which is then connected to the vacuum system.

The Marchuk tube is then processed by vacuum bakeout for over a week. The tube is baked at approximately 250 C with IR lamps. The anode and cathode were outgassed by resistance heating 2500 K for 3 hours and each probe was outgassed above its expected operating temperature of 1600 K. The ultimate pressure for this processing is 10^{-8} torr or lower.

The cesium reservoir was formed by breaking a 2 gm cesium ampoule during the processing. The ampoule was loaded under an argone overpressure with a very high purity, 99.995%. A simple iron weight activated by a magnet was dropped on the ampoule to open the cesium in the reservoir. The cesium ampoule was opened after all high temperature processing was completed, and the ultimate pressure was restored by vac-ion pumping to 10^{-8} torr.

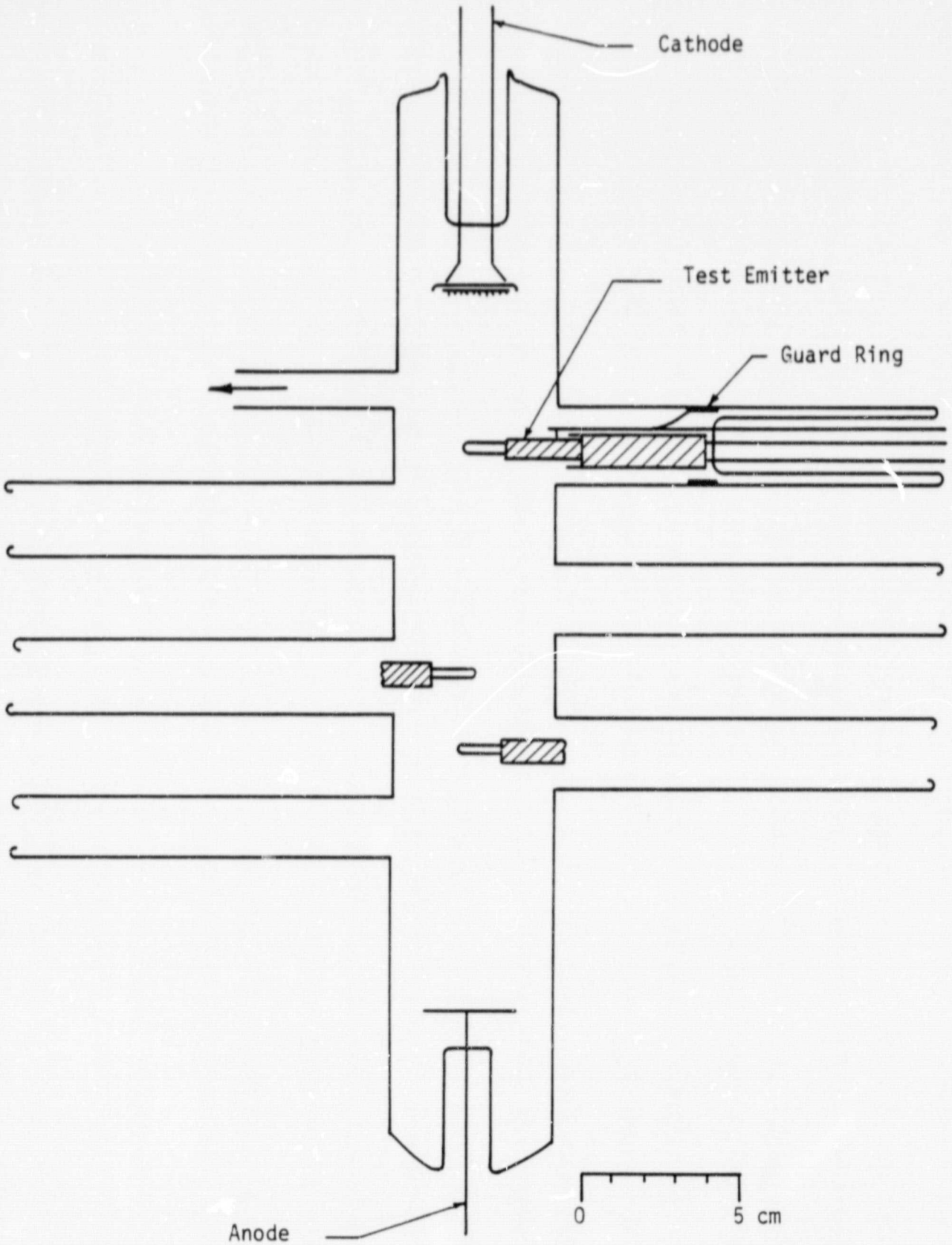


FIGURE 7 EXPERIMENTAL TUBE

The tubes were sealed off from the vacuum chamber by melting a section of the glass lead tube and fusing it.

Thoriated tungsten samples were purchased and are ready to be installed in a second Marchuk tube. Both 1% and 2% thorium alloys have been obtained. This effort was the primary effort for the final funding period. The LaB_6 measurements were terminated with the failure of the last tube. The thoreim alloy tests are being completed after program termination. Repeated tube failures kept us from meeting the schedule.

Plasma Anode Measurement Technique

Fig. 8 shows the experimental circuit and defines the variables of interest. All circuitry to the left of the tube relates to the production and maintenance of the main discharge, and all circuitry to the right of the tube relates to probe measurements. Probe current measurements, with the gross emission I_p, are made for steady state conditions. The probe heating current is I_f. With $I_f = 0$ (cold probe) the probe acts like a typical Langmuir probe. For a probe voltage, $V_p < \sim -10$ volts I_p is all ion current from the plasma. Below this value of V_p, the probe collects plasma electrons thus destroying the ion sheath at the surface. As the probe is heated, electrodes are emitted and I_p changes, going through a maximum and subsequently decreasing. The current with $I_f = 0$ is I_{po}, and the electron current from the probe is then $I_p - I_{po}$ (for $V_p < -10$ volts). This is defined as I_e. The slight increase in I_p with increasingly negative voltage V_p is due to anomalous Schottky effect.

The discharge parameters are set to produce a plasma with no apparent instabilities at the anode. Initially, curves with V_p vs. I_p for varying I_f are produced for each probe. V_p is chosen by inspection of the I-V characteristic such that for $I_f = 0$, the ion current is saturated. This generally produces a V_p value about 5 to 6 volts more negative than the probe floating potential (V_p value where $I_p = 0$). Subsequent probe data are taken at this value of V_p.

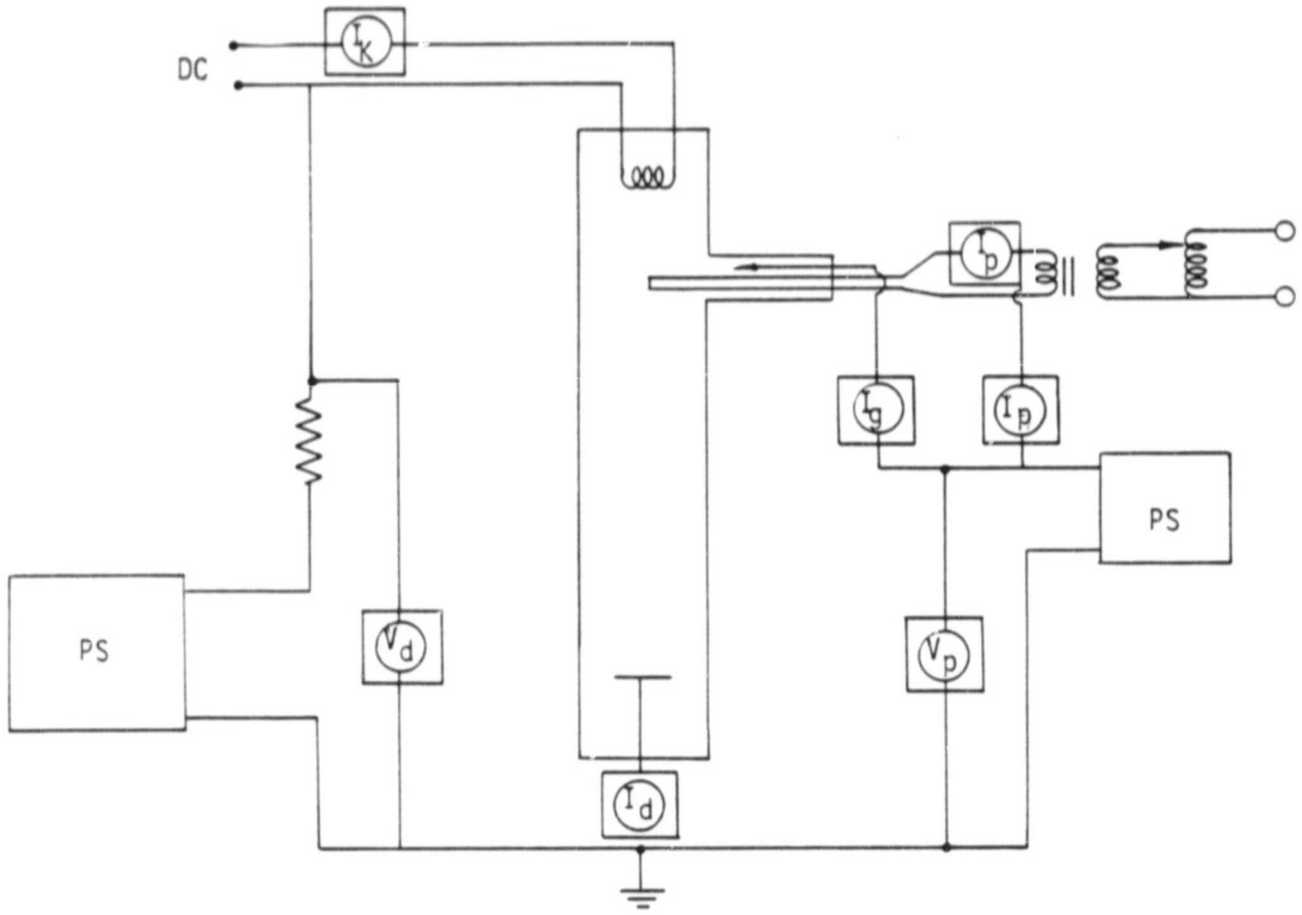


FIGURE 8 EXPERIMENTAL CIRCUIT SCHEMATIC

With the V_p value fixed, I_f is varied to change the probe temperature. Prior to the measure of I_p, the probe temperature is allowed to equilibrate.

Plasma Anode Experiments

After vacuum processing the Marchuk tube was sealed off and set up in an oven. All the electronic circuitry were connected to the tube and the cesium reservoir was immersed in a mineral-oil bath. Heater tapes were used to prevent cold spots on the elbow section of the reservoir. Temperatures in the reservoir and oven were monitored with conventional mercury thermometers.

To begin the experiment, the oven and the cesium reservoir were first heated up. The latter at 412 K and the former about 15 higher. This was to vaporize the cesium into the main tube and preventing condensation on the sides with a slightly higher temperature. At the right temperatures, the emitter was first heated with an arbitrary current. The cesium plasma was then ignited by setting a voltage between the emitter and collector.

In the first tube, the emitter did not light immediately up although it did before vacuum processing. It was noted that the current was fairly high (~15A) and the voltage was low (~3V). This did not correspond to previous measurements of the emitter resistance. The suspected cause was a short in the tungsten filament itself. Attempts to break the contact by switching on and off an alternating current to induce an electric/magnetic field succeeded. However, this generated an excessive amount of thermal stress on the tungsten lead-throughs causing the glass seal to crack. The resulting leakage caused the cesium to be oxidized.

All sections of the contaminated Marchuk tube except the collector were cut away from the main tube body. The emitter had to be redesigned and a new reference probe was put in and a new cesium

reservoir connected. The two LaB_6 probes were taken out to prevent the coating from contamination and flaking.

In the second tube a rhenium wire was used as the references probe. The glass-blower encountered cracks when he tried to join this section to the main body. He decided then to put it in the oven and annealed it. In doing so, he oxidized the collector disc and the rhenium wire. They had to be taken out and cleaned and replaced.

When the emitter was examined, it was found that the cause of the short and the resultant failure of the experiment was due to the tantalum radiation shield sagging under intense heat and consequently touching the tungsten spiral. The second time, tantalum rods were used to support both ends of the shield. It was tested in a vacuum bel-jar and performed as it should. A new glass blower was found in order to complete the tube reassembly in a timely manner.

Mr. J.S. Whang of Siltronics, Tempe, agreed to reassemble the Marchuk tube. He also encountered many cracks when he was assembling the sections. He suggested that the main tube was still liable to crack.

The rebuilt Marchuk tube was then hooked up to the vacum system for vacuum processing and bake-out. After one week it was sealed off. Prior to placing it in the oven, it was noticed that the cesium had changed color. A very small crack was discovered at the bottom part of the tube, near the collector.

After this failure no time remained during the contact schedule to complete the LaB_6 work.

During the same period of time work was done to make a set of parts for thoriated tungsten emission measurements. The materials were obtained in August and all the parts have been accumulated for two or three tubes.

1720 Aluminosilicate glass was ordered from electronic Glass Suppiy Company to be used as the envelope of the marchuk tube. The higher bake out temperature of the glass as compared to 3320 Uranium glass allows a large extension of the operating temperature range of the experiment.

Direct sealing of tungsten leadthroughs to this glass as advertised to be possible was proved to be unsatisfactory. 3320 Uranium glass is therefore still chosen as the material for the pressed seal. The transition from 1720 to 3320 glass was tested to be satisfactory.

Both the pressed seals and the main body of the marchuk tube shall be prepared by Siltronic Co. The tungsten wire leadthrough holders for making the pressed seals were made by the ASU Engineering machine stop.

Tungsten emitters in the shape of counterwound pancake filaments were prepared by Union City Filament Co. The tantalum shield for the tungsten filament emitter was found to be best supported by tantalum rods attached to the tungsten leadthroughs. This arrangement will minimize the possibility of having the tantalum shield making contact with the filament, and thus short out the emitter circuit. 1% thoriated tungsten wiretest sample were supplied by H-Cross Co., and 2% thoriated tungsten wire were obtained from Thermionic Products Co. The molydenum bushings and the ceramic rods are ready to be used in the fabrication of the testing sample electrodes. Cesium ampoule and magnetic breaking rod are also ready to be placed in the Marchuk tube.

Testing will be carried on after the program termiantion.

Photon Counting Pyrometer

A photon counting pyrometer has been designed and built which will permit black body temperatures to be determined with a precision of $\pm$0.2K. The basic concept and design were originated by Dr. Edmund

Storms at the Los Damos Scientific Laboratory. Several parts were generously supplied by Dr. Storms. Other equipment was obtained form laboratories in the Engineering Department at A.S.U.

In the measurement of quantized radiation fields such as light, most information is obtained by counting individual events corresponding to the individual photons. The counter can be compared to a d.E. Analog technique for making light measurements where many photon events are integrated over time, with the result that the photon counting method in a high performance system has at least three major advantages:

a) optimum signal to noise ratio for quantum-limited signals
b) excellent long-term stability
c) wide linear dynamic range

Precision is improved by more than an order of magnitude and repeatability is greatly enhanced when comparing the photon counter to optical pyrometry.

An available Leeds and Northrup pyrometer was modified as shown in Fig. 9. Light from a black body source passes through a narrow band interference filter and is focused onto the metal mirror through the objective lens system. The hohlrom image, where the temperature is to be measured, is focused onto the metal mirror through the objective lens system. The hohlrom image, where the temperature is to be measured, is focused over the 0.010 cm hole in the mirror. This is done while viewing the image and mirror through the image lens system. The light passing through the mirror hole is attenuated by a choice of neutral density filters, before continuing to the photomultiplier tube. Pulses from the photomultiplier tube are amplified, clipped, and reamplified by a P.A.R. 1121 Amplifier-System. They are then fed to a Hewlett-Packard 5308A counter. The overall schematic is shown in Fig. 10.

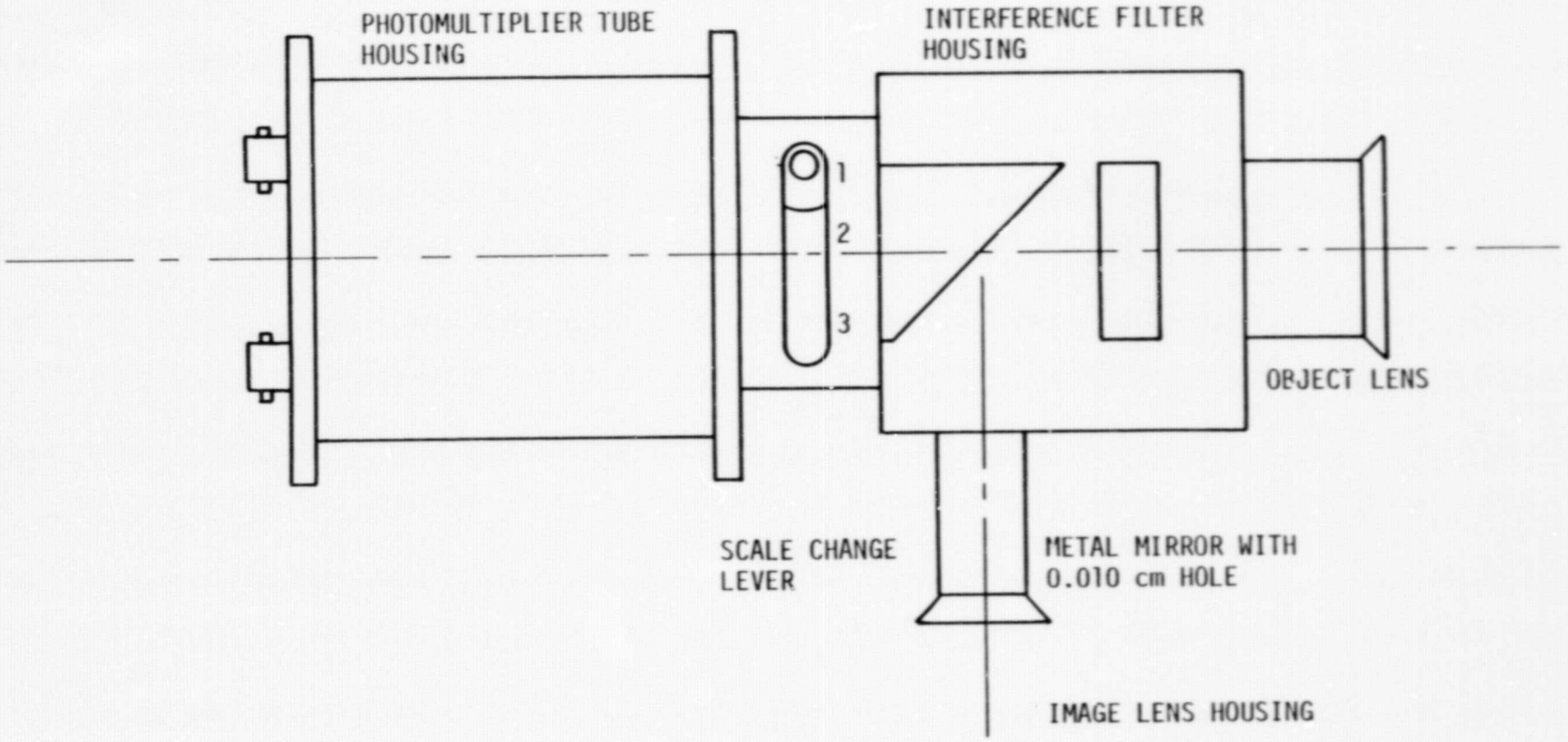


FIGURE 9 TOP VIEW OF PHOTON COUNTING PYROMETER.

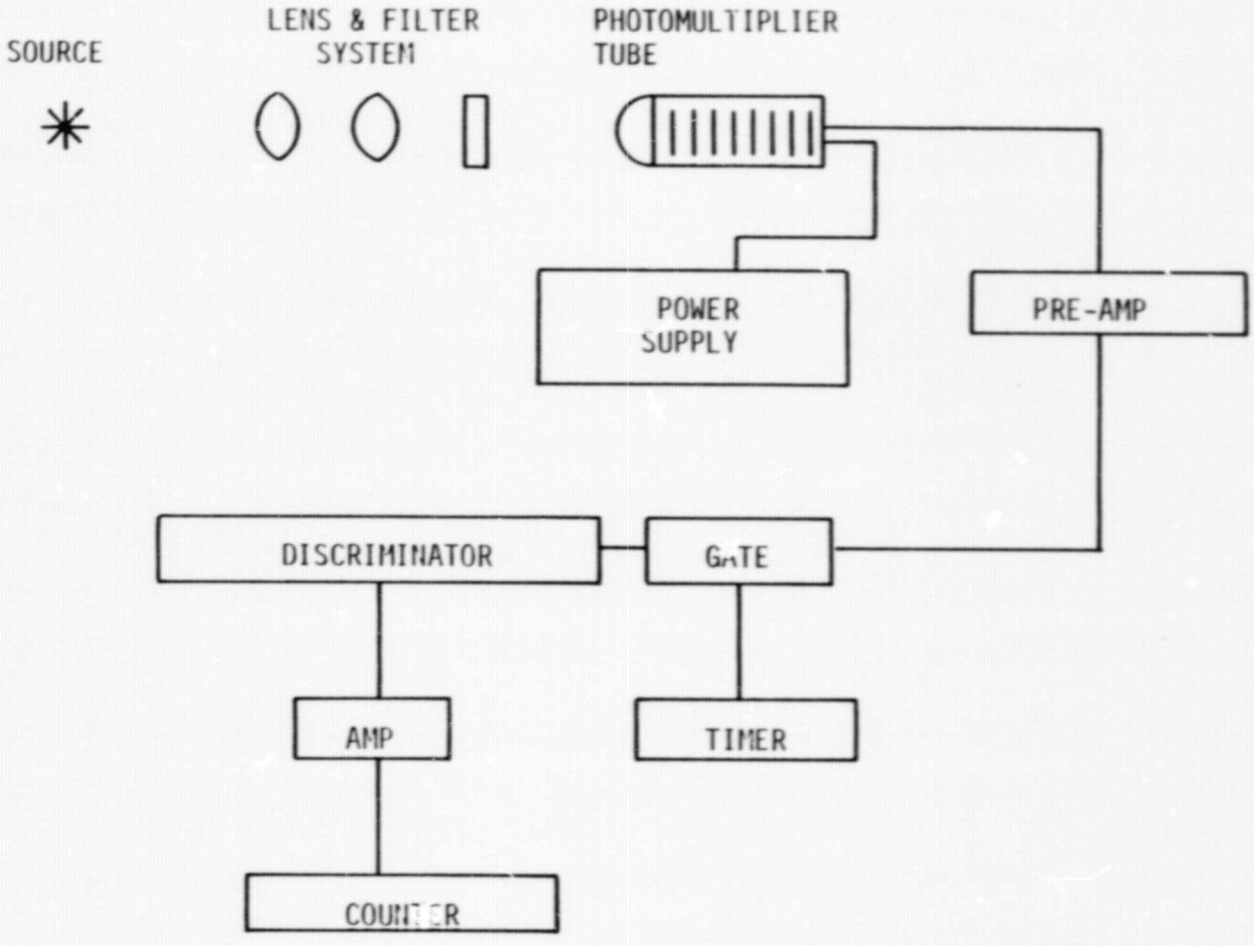


FIGURE 10 PHOTON COUNTER SCHEMATIC

Calibration of the pyrometer requires knowledge of the count rate (R_g) at a known temperature (T_g), the wavelength of the transmission maximum in the interference filer $(\gamma_0)_1$ and Planck's second radiation constant (C_2). L.A.S.L. has offered to let us use their gold furnace for calibration. Planck's law related the count rate, R_c, and the unknown temperature, T_m, through the equation

$$T_m = 1/[(\ln R_g - \ln R_c)\ \gamma_0/C_2 - 1/T_g]$$

where $C_2 = 0.014388$ mk

$1/T_g = 7.4762 \times 10^{-4} k^{-1}$

The measurements are based upon extrapolation of the thermodynamic temperature scale above the gold point and the absolute accuracy is thus, in principle, as good as can be obtained. The interference filter has a finite bandwidth, and with the limits of accuracy in the electronics system and elsewhere, the precision is calculated to be better than $\pm$0.2K at 2000K.

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2. Buckingham, J.D., ''Thermionic Emission Properties of a Lanthanum Hexaboride/Rhenium Cathode,'' Brit. J.j Appl. Phys., 1965, Vol. 16.